

**Problem Set 2 - 2.1, 2.6, 2.11, 2.26, 2.34, 2.35****2.1 (a)**  $\Delta H_{vap} = 2447 \text{ kJ/kg}$ , then

$$q = (1 \text{ L H}_2\text{O}) \left( \frac{1 \text{ kg H}_2\text{O}}{1 \text{ L}} \right) (2447 \text{ kJ/kg}) = 2447 \text{ kJ}$$

**(b)**  $C_{\text{H}_2\text{O}} = 4 \text{ J/}^\circ\text{C} \cdot \text{g} = 4 \text{ kJ/}^\circ\text{C} \cdot \text{g}$ ,

$$(2447 \text{ kJ}) \left( \frac{1^\circ\text{C} \cdot \text{kg}}{4 \text{ kJ}} \right) \left( \frac{1 \text{ hiker}}{60 \text{ kg}} \right) = 10^\circ\text{C}$$

**(c)**  $C_{12}H_{22}O_{11}(g) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l)$ 

$$\Delta H = \{11(-285.8 \text{ kJ/mol}) + 12(-393.5 \text{ kJ/mol})\} - \{-2222.1 \text{ kJ/mol}\} = -5644 \text{ kJ/mol}$$

The molecular weight of sucrose is  $12(12 \text{ g/mol}) + 22(1 \text{ g/mol}) + 11(16 \text{ g/mol}) = 342 \text{ g/mol}$ , then

$$2447 \text{ kJ} \left( \frac{1 \text{ mol sucrose}}{5644 \text{ kJ}} \right) \left( \frac{342 \text{ g}}{1 \text{ mol}} \right) = 148 \text{ g}$$

**2.6 (a)** 100 g  $H_2O(l)$  heated from  $T = 0^\circ\text{C} \rightarrow 100^\circ\text{C}$  at 1 atm,

$$C_p^{(H_2O)} = 4 \text{ J/}^\circ\text{C} \cdot \text{g}$$

$$q = (100 \text{ g})(100^\circ\text{C} - 0^\circ\text{C})(4 \text{ J/}^\circ\text{C} \cdot \text{g}) = 40 \text{ kJ}$$

which is positive, since heat is put in.

**(b)** 100 g  $H_2O(l)$  frozen at  $0^\circ\text{C}$  at 0.01 atm

$$\Delta H_{\text{fusion}}^{(H_2O)} = (6 \text{ kJ/mol}) \left( \frac{1 \text{ mol}}{18 \text{ g}} \right) = 333 \text{ J}$$

Since we are freezing the water, by convention the sign is negative (taking heat out), and

$$q = (-333 \text{ J/g})(100 \text{ g}) = -33.3 \text{ kJ}$$

**(c)** 100 g  $H_2O(l)$  evaporated to steam at  $100^\circ\text{C}$ , 1 atm,

$$\Delta H_{\text{vap}}^{(H_2O)} = (40.7 \text{ kJ/mol}) \left( \frac{1 \text{ mol}}{18 \text{ g}} \right) = 2.26 \text{ kJ/g}$$

$$q = (2.26 \text{ kJ/g})(100 \text{ g}) = 226 \text{ kJ}$$

**2.11** 1 mol  $H_2O(l)$  at  $100^\circ\text{C}$ , heated until completely vaporized. Calculate  $q, w, \Delta E, \Delta H$ .**(a)** In a cylinder,  $p_{ex} = 1 \text{ atm}$ 

$$V_{gas} = \frac{nRT}{p} = \frac{(1 \text{ mol})(8.2 \times 10^{-2} \text{ L} \cdot \text{atm/K} \cdot \text{mol})(373 \text{ K})}{(1 \text{ atm})} = 30.6 \text{ L}$$

$$V_{liquid} = (1 \text{ mol } H_2O) \left( \frac{18 \text{ g}}{1 \text{ mol}} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ g}} \right) = 0.018 \text{ L} \approx 0$$

$$w = -p_{ex}\Delta V = -(1 \text{ atm})(30.6 \text{ L}) \left( \frac{101 \text{ J}}{\text{L} \cdot \text{atm}} \right) = -3.09 \text{ kJ}$$

$$\Delta E = q + w = (-3.09 \text{ kJ}) + (40.7 \text{ kJ}) = 37.6 \text{ kJ}$$

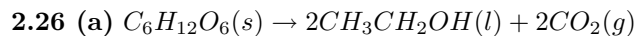
$$\Delta H = q_{p=\text{const}} = 40.7 \text{ kJ}$$

(b)

$w = 0 \leftarrow$  expansion against a vacuum

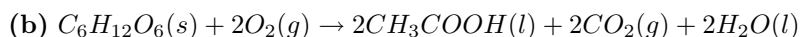
Since  $\Delta E$  and  $\Delta H$  are state functions, they are path independent, and so we may use the values from the previous section, giving

$$\Delta E = 37.6 \text{ kJ} = q; \Delta H = 40.7 \text{ kJ}$$

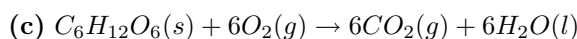


$$\Delta H_{rxn} = \sum \Delta H(\text{products}) - \sum \Delta H(\text{reactants})$$

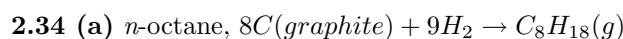
$$\Delta H_{rxn}^{EtOH} = \{2(-277 \text{ kJ/mol}) + 2(-394 \text{ kJ/mol})\} - \{-1274 \text{ kJ/mol}\} = -68 \text{ kJ/mol}$$



$$\Delta H_{rxn}^{AcOH} = \{2(-484 \text{ kJ/mol}) + 2(-394 \text{ kJ/mol}) + 2(-286 \text{ kJ/mol})\} - \{-1274 \text{ kJ/mol}\} = -1054 \text{ kJ/mol}$$



$$\Delta H_{rxn}^{combust} = \{6(-394 \text{ kJ/mol}) + 6(-286 \text{ kJ/mol})\} - \{-1274 \text{ kJ/mol}\} = -2806 \text{ kJ/mol}$$

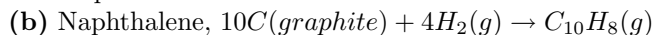


$$\Delta H_f = \{8(C - C_{\text{graphite}}) + 9(H - H)\} - \{7(C - C) + 18(C - H)\}$$

Remember, it takes energy to break bonds (by convention, +) and energy is released when bonds are made (by convention, -). Substituting in the appropriate values,

$$\Delta H_f = \{8(717 \text{ kJ/mol}) + 9(436 \text{ kJ/mol})\} - \{7(344 \text{ kJ/mol}) + 18(415 \text{ kJ/mol})\} = -218 \text{ kJ/mol}$$

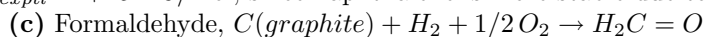
The experimental value is  $-208 \text{ kJ/mol}$ , which is pretty good, considering the approximation of using average bond enthalpies.



$$\Delta H_f = \{10(C - C_{\text{graphite}}) + 4(H - H)\} - \{5(C = C) + 6(C - C) + 8(C - H)\}$$

$$\Delta H_f = \{10(717 \text{ kJ/mol}) + 4(436 \text{ kJ/mol})\} - \{5(615 \text{ kJ/mol}) + 6(344 \text{ kJ/mol}) + 8(415 \text{ kJ/mol})\} = +455 \text{ kJ/mol}$$

$\Delta H_{exptl} = +151 \text{ kJ/mol}$ , since naphthalene is more stable due to resonance effects.



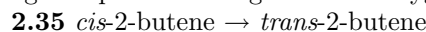
$$\Delta H_f = \{(717 \text{ kJ/mol}) + (436 \text{ kJ/mol}) + 1/2 (498 \text{ kJ/mol})\} - \{2(415 \text{ kJ/mol}) + (725 \text{ kJ/mol})\} = -153 \text{ kJ/mol}$$

$\Delta H_{exptl} = -116 \text{ kJ/mol}$ , the average-bond enthalpy approximation is most valid in the large-molecule limit.



$$\Delta H_f = \{(717 \text{ kJ/mol}) + (436 \text{ kJ/mol}) + (498 \text{ kJ/mol})\} - \{(415 \text{ kJ/mol}) + (725 \text{ kJ/mol}) + (350 \text{ kJ/mol}) + (463 \text{ kJ/mol})\}$$

$\Delta H_f = -302 \text{ kJ/mol}$ ,  $\Delta H_{exptl} = -379 \text{ kJ/mol}$ , discrepancy due to resonance effects, with the hydroxyl hydrogen capable of being on either oxygen.



$$\Delta H_{cis \rightarrow trans} = \Delta H_f^{(trans)} - \Delta H_f^{(cis)} = (-11.1 \text{ kJ/mol}) - (-7.0 \text{ kJ/mol}) = -4.1 \text{ kJ/mol}$$

So we see that the *trans* configuration is more stable than the *cis* configuration, this is known as the "*trans*-effect".